

November 8, 1939

Professor Charles D. Hurd  
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Dear Professor Hurd:

I have just read your very interesting paper in the August J. Am. Chem. Soc. on cyclooctatetrene, and inspired by it and other recently expressed doubts I have taken out my old reprint and tried to think back to the original work.

Taken in the abstract, I do not see how anyone could disagree with you as to the many possible directions that could be taken by the reactions used by Willstatter and his coworkers in arriving at cyclooctatetrene. There are, however, certain analogies and observations, also the experimental conditions used, which limit the possibilities.

First, there is the older work of Willstatter on tropilidene, Ann., 1901, 317, 204, in which the conjugated cycloheptatriene system seemed to be preferentially formed. Then there is the narrow boiling range, 0.5°, of cyclooctatriene dibromide, indicating the preferential formation of a single isomer, which would most reasonable be by 1,6 addition. Third, all reactions were carried out at as low temperatures as possible, and in the final Geryk-vacuum demethylation a more stable product was obtained than at higher temperatures. I thi

I think, therefore, that it is hardly fair to compare this procedure with the outcome of "pyrolyses" at over 200°, where rearrangements might easily occur.

Also, I do not see how you can say that "the fact that none of the conjugated hydrocarbon came from IX..." casts doubt on the structure of cyclooctatetrene. I should consider it good negative evidence in favor of Willstatter's formulation if even drastic pyrolysis failed to produce a conjugated system which would not be expected to form directly on structural grounds. As for the result with X, the diquaternary compound leading to

the tetraene was not a 1,2 isomer, and this might easily influence the result. Could it not be repeated with the 1,4 isomer? And might not the percentage of butadiene even from X have been much larger if the decomposition had been run more comparably according to our directions for the cycloocta-compound.

I am very glad that these questions are being re-examined, and only interesting results can come to light, whatever the final result. But I do feel that the original work, too, was carried out on a basis carefully reasoned according to the knowledge of the time, and that doubt arising from reactions occurring at at temperatures 100° higher, or even 300° higher, as has been done in certain catalysis experiments, should be examined in the same spirit of skepticism.

Looking forward to your comments, and hoping you are planning additional experiments,

Sincerely,

Michael Heidelberger

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